



# On force fields for molecular dynamics simulations of crystalline silica



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## ARTICLE INFO

### Article history:

Received 26 March 2015

Received in revised form 14 May 2015

Accepted 16 May 2015

Available online 3 June 2015

### Keywords:

MD simulations

Force fields

Potentials

Crystalline silica

Phase transition

Computation time

## ABSTRACT

This paper reviews and examines interatomic potentials or force fields for molecular dynamics (MD) simulation of crystalline silica. The investigated potentials are the BKS, Pedone, Munetoh, TTAM, and CHIK. The calculated values of the lattice constants, density, radial and bond-angle distribution functions, equations of state, and phase transitions using different potentials are compared to experimental values for polymorphs of silica: quartz, cristobalite, coesite, and stishovite. Simulation results with the BKS potential accurately predict the experimental measurements to within 2%, and converge within a reasonable timeframe on an average workstation. The Pedone potential, also parameterized for other metallic oxides, computationally is slightly more expensive and is not as accurate. The simulations with both the CHIK and TTAM potentials are less accurate than with the BKS potential for modeling silica over the entire range of the phase diagram. The simulations with the Munetoh potential are by far the cheapest in terms of the modest computational requirements, but unsuitable for modeling crystalline silica. It could not produce the nature of the  $\alpha$ - $\beta$  and I-II phase transitions in quartz or the equation of state for stishovite silica, and the predicted structural properties sometimes differ from experimental values by more than 10%.

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## 1. Introduction

Molecular dynamics (MD) simulations are an effective tool for characterizing atom–atom interactions and determining the material properties by averaging the results over simulation times of 10–100 s of picoseconds. Recent advances in materials science at the nano- and micro-scales, including methods for atoms self-assembly, have inspired the interest in simulating atomic interactions for designing and engineering new materials and composites with superior performance and characteristics [1,2]. The ability to successfully simulate atomic interactions, and extract the material properties at the nano- and micro-scale and relate them to the bulk material properties offers unlimited opportunities for developing new materials and modifying material properties through the manipulation of atoms. The recent interest in MD simulations and exploring its potential have created an opportunity for investigating material properties at the atomic scale and relating them to those at the macro-scale. This has been possible through

the continuing leaps in computing capabilities at progressively lower costs [3,4].

Simulating atom–atom interactions using improved algorithms is at the forefront of computational materials science. MD simulations have been used in a myriad of investigations in many fields, including physics, chemistry, biology, engineering, aerospace, bio-engineering, pollution, drug delivery, etc. Specific examples are materials self-assembly, interactions of proteins and ligands, selection of additives for improving the mechanical and surface properties, and radiation hardening of materials for uses in space, medical, diagnostics, drug delivery, and nuclear reactors [1,2,5,6].

In computational materials science, there are two distinct methods for describing atom–atom interactions, namely: (a) Ab Initio Molecular Dynamics (AIMD), and (b) Classical Mechanics (hereafter referred to as MD). Both methods model the time evolution of the atom–atom interactions and help extract the dynamic, thermodynamic, and structural properties of the materials. MD simulations typically consist of a data file of the initial coordinates of the atoms of interest, and a method or force field for characterizing the atom–atom interactions. The accuracy of the simulation results, typically defined by the user, depends on the approximations used in calculating the trajectories of the atoms. The trajectories are generated by numerically integrating Newton's equations

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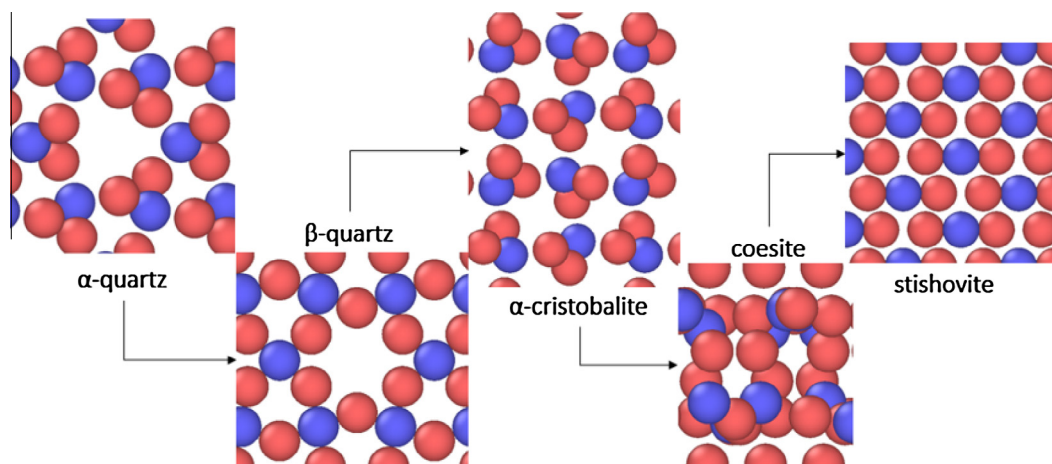


Fig. 1. Crystalline phases of silica reviewed in this paper.

of motion and the atom–atom interactions are characterized by interatomic “potentials” (also known as force fields). These potentials are typically fitted to experimental data or high-level AIMD simulation results.

In the late 1950s, Alder and Wainwright [7,8], pioneers in the field of MD, have studied the interaction of hard spheres. However, it was not until 1964 that the first potential to produce realistic results was used to model liquid argon [9]. Still, the first credible simulation that accurately reproduced the water properties took place in 1974 [10].

The early successes of MD simulations have inspired the development of an exhaustive list of pair and many-body potentials, with terms to account for the various interactions, such as those due to van der Waals, Coulomb, bond, bend, and dihedral angle [11]. The different ways for expressing the atom–atom interactions resulted in a diverse list of potentials. For instance, incorporating the Coulomb interactions with fixed charges is typically associated with solvers such as Ewald [12] or particle–particle particle-mesh (PPPM) [13]. However, some have used dynamic charges, which often incorporate the electronegativity equilibration (QEq) scheme (or a derivative) developed by Rappé and Goddard [14] to calculate the self-charges on the atoms. Still, others have elected to neglect the Coulomb interactions altogether in the simulations that do not require them for decreasing the computation times of the simulations. Choosing between a pair-potential and a many-body potential, and the manner of accounting for the Coulomb interactions, is often a compromise between accuracy, transferability, and computational cost.

A shortcoming of the MD simulations is the limited transferability to various regions of the materials phase diagram. This is because the potentials used in the simulations are typically not fitted to the experimental data in all these regions. In addition, MD simulations do not accurately model the changes in the chemical bonding because of neglecting the effects of quantum chemical electronic polarization. When the materials undergo transformations to other polymorphs, the empirically derived potentials may not perform well; the QEq [14] empirical scheme attempted to mitigate this concern. Another limitation of the MD simulations is when incorporating several materials into a single model or including many-body effects. Both of these cases would increase the computational time and hardware requirements, impeding the chance to obtain acceptable results in a reasonable timeframe.

Notwithstanding the aforementioned limitations, MD simulations are highly recognized for the ability to effectively describe the atom–atom interactions, with successful applications to all sorts of materials, including carbon nanotubes, biomolecules,

hydrocarbons, and metallic oxides to name a few. Among the most widely investigated materials with MD simulations is silica. It has wide uses in the fabrication of computer wafers and microprocessors, and the development of advanced instrumentation for diagnostics and data acquisition devices in research, and many medical and industrial applications. Examples are biomedical [15,16], photonics [17], nuclear-targeted drug-delivery [18], fused silica optics [19–22], and micro/nano-electronics as nano-composite films [23,24], blue-light emitters [25], and waveguides [26]. The Si/SiO<sub>2</sub> interface, an integral part of transistors development that directly affects the insulation and dielectric properties has been investigated [27]. Therefore, it is important to understand and characterize the nano-scale properties of silica and review various potentials and develop a short list of the most promising potentials for MD simulations of silica.

The objective of this work is to review proposed potentials for MD simulations of crystalline silica; namely, quartz, cristobalite, coesite, and stishovite (Fig. 1), and to determine the appropriate ones with emphasis on the computational cost, the accuracy of the results compared to experiments, and transferability.

The following section reviews many of the developed potentials for MD simulations of silica including those by van Beest et al. [28], Pedone et al. [29], Munetoh et al. [30], Tsuneyuki et al. [31], and Carré et al. [32]. These potentials will hereon be referred to as BKS [28], Pedone [29], Munetoh [30], TTAM [31], and CHIK [32], respectively. It is important to note that the Pedone potential models a whole class of oxides and thus its transferability to modeling more complex materials is one of its key advantages, compared to other potentials (Figs. 2 and 3). The TTAM potential, a precursor to BKS, is not extensively reviewed. Additionally, the CHIK potential, primary fitted for modeling amorphous silica, is excluded from some of the calculations in this paper.

## 2. Potentials for MD simulation of silica

For silica, the Si–O bonds can be characterized as both covalent and ionic. The ionicity is due to the electronegative atoms, whereas the covalency is developed through bond-angles. It has been shown that the contributions of the electronegativity are an order of magnitude higher than those of the short-range forces, such as bond-angles [33]. Therefore, it is imperative that the potentials for MD simulations include the Coulomb forces in order to provide an accurate description of silica. Owing to the complex nature of the covalent/ionic Si–O bond, several potentials attempted to provide a sound physics model [34].

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